Australian Government
Department of Defence
Defence Science and
Technology Organisation

Catalytic Degradation of Methylphosphonic Acid Using Iron Powder/ Iron Oxides

Joseph John Moniodis[#], John Webb[#], Gary Mathys[†],
Harry Rose[*] and Robert Mathews[*]

[#]Murdoch University, Western Australia

[†]Maritime Platforms Division
Defence Science and Technology Organisation

[*]Human Protection and Performance Division
Defence Science and Technology Organisation

DSTO-TR-1849

ABSTRACT

The catalytic degradation of methylphosphonic acid, the final hydrolysis product of some nerve agents, using Fe, Fe_2O_3, $FePO_4$ and Al/Al_2O_3 was studied by evolved gas analysis - Fourier transform infrared spectroscopy (EGA-FTIR) under nitrogen, air and oxygen atmospheres. All of the compounds catalysed the reaction to some extent (in comparison to heating MPA alone) with Fe_2O_3 being the best catalyst with carbon-containing gases evolving at 375°C under all atmospheres. Temperatures of formation of carbon containing gases using the other catalysts were 400-450°C for Fe, 400-425°C for FePO4 and ca. 510°C for Al/Al_2O_3. There is some evidence that Fe and Fe_2O_3 reacted with MPA to form an iron phosphate species, which further catalysed the reaction although to a lesser extent.

RELEASE LIMITATION

Approved for public release

Catalytic Degradation of Methylphosphonic Acid Using Iron Powder/ Iron Oxides

Executive Summary

The destruction/degradation of chemical warfare agents (CWAs) has been an ongoing challenge for States Parties to the Chemical Weapons Convention (CWC), which requires that chemical weapons be destroyed in an "essentially irreversible way to a form unsuitable for production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such." For nerve agents such as Sarin, Soman and VX, this requirement may only be satisfied through cleavage of the P-C bond. The most common method of destruction of CWAs is incineration but this method is not always suitable because of the high capital costs involved and public opposition to the process based on health and environmental issues. This has led to research to find more reliable and environmentally acceptable methods of destruction of CWAs. A majority of the studies conducted to date have involved the use of various metals and their oxides as catalysts and the use of dimethyl methylphosphonate (DMMP) as the non-toxic chemical agent simulant.

The present study investigates the use of temperature-programmed evolved gas analysis - Fourier transform infrared spectroscopy (EGA-FTIR) to assess the catalytic effect of iron oxide, iron phosphate, iron powder and aluminium/aluminium oxide on the degradation of methylphosphonic acid (MPA), the final hydrolysis product of most nerve agents. EGA-FTIR provides simultaneous measurement (in the mid-infrared frequencies) of volatile products which enable characterisation of the decomposition processes. This allows detection and identification of multiple products by monitoring characteristic absorption bands of individual species over the thermal cycle thus providing evolution profiles of gaseous products.

The potential of the EGA-FTIR technique to be used in catalytic degradation studies has been demonstrated. The oxides used in this study all catalysed the decomposition of MPA (compared to heating the MPA alone), with Fe_2O_3 giving the best results as demonstrated by the lower temperature of gas evolution. Several avenues for further investigation have been identified based on this preliminary work.

Contents

1. Introduction

The Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction (CWC) specifies that all chemical weapons stockpiles of States Parties must be destroyed within 10 years after its entry into force.[1] The most common method of destruction of chemical warfare agents (CWA) is incineration but this method is not always suitable because of the high capital costs involved and public opposition to the process based on health and environmental issues.[2]

Earlier work conducted during an Honours project at Murdoch University [3] in collaboration with Defence Science and Technology Organisation (DSTO) explored the science of metal oxide degradation of CWA simulants to get a better understanding of the processes taking place and to gain an insight into the mechanisms of these processes. The results of this study were promising and continued research in this area may result in the use of this technology for destruction and decontamination purposes.

Evolved gas analysis - Fourier transform infrared spectroscopy (EGA-FTIR) has been shown to be a valuable technique for decomposition studies because it provides simultaneous measurement of sufficient volatile products to characterise decomposition processes.[4] The simultaneous measurement of all mid-infrared frequencies by FTIR allows detection and identification of multiple products by the monitoring of characteristic absorption bands of individual species over the thermal cycle; this provides evolution profiles of gaseous products. The use of EGA-FTIR at DSTO has been reported previously in the study of environmental degradation of pyrotechnic magnesium powder [6], polymer degradation studies [5] and identification of polyurethanes.[7] EGA-FTIR has been used in this study because of its potential to give insight into degradation processes that may be occurring leading possibly to improvements in destruction and decontamination techniques.

The CWC requires that chemical weapons be destroyed in an "essentially irreversible way to a form unsuitable for production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such."[1] The aim of this study is to investigate the catalytic degradation of methylphosphonic acid (MPA, Figure 1), the final hydrolysis product of most nerve agents, with iron oxide, iron phosphate and iron powder, as well as aluminium/aluminium oxide, using temperature programmed EGA-FTIR. Since MPA is a Schedule II chemical the above requirement can only be met through breakage of the P-C bond.
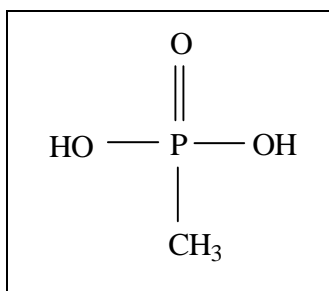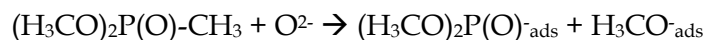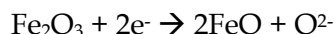
$$HO - \overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle CH_3}{|}}{P}} - OH$$

Figure 1 – methylphosphonic acid (MPA)

2. Background

Catalytic degradation studies for the destruction of CWA have, for the most part, focussed on using metals and their oxides [13-24] as catalysts, and the use of dimethyl methylphosphonate (DMMP) as the non-toxic chemical agent simulant. Templeton and Weinberg [18;19] undertook one of the earlier studies in 1985 where they examined the adsorption and decomposition of phosphonate esters (including DMMP) on aluminium oxide films. It was found that DMMP adsorbed dissociatively in low (sub-monolayer) surface coverages at 22°C by cleavage of the P-OC bond and that the P-C bond remained intact even at high temperatures. Since then a number of different metal oxides have been studied as possible catalysts for the destruction of CWA simulants including copper, vanadium, nickel, aluminium, magnesium, manganese, lanthanum and titanium oxides.[13-25] Metals including nickel, palladium, rubidium, molybdenum, aluminium and platinum [8-12;26] have also been studied as well as Cu-substituted hydroxyapatite [27]. A comprehensive review of the surface chemistry of organophosphonates has been carried out by Ekerdt *et al*.[28]

The use of iron oxides as catalysts for the degradation of organophosphorus compounds have been studied by a number of authors.[20-24] Mitchell *et al*.[20;21] observed P-C bond cleavage at room temperature when DMMP is adsorbed on iron oxide. The cleavage is a result of the low energy pathway provided by the Fe(II)/Fe(III) redox couple where iron oxide reacts according to the Mars and Van Krevelen mechanism:

$Fe_2O_3 + 2e^- \rightarrow 2FeO + O^{2-}$

$(H_3CO)_2P(O)\text{-}CH_3 + O^{2-} \rightarrow (H_3CO)_2P(O)^-_{ads} + H_3CO^-_{ads}$

$2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3$

When studying the degradation of DMMP on clean Fe_2O_3 Henderson *et al*. [23] found that the P-CH$_3$ bond was oxidised by the lattice oxygen resulting in a fully coordinated phosphorus species. Interestingly, at temperatures above 377°C, the surface phosphorus species migrated to the bulk of the oxide leaving the surface available for further DMMP decomposition. In a related study [22], this group found that coadsorbed water led to more DMMP decomposition, but this decomposition was most likely due to hydrolysis, which does not break the P-C bond.

Cao *et al*. [23] also studied the thermocatalytic oxidation of DMMP on several metal oxides, including iron oxide. They found vanadium oxide to be the best catalyst because the other oxides tended to react with the by-products of the reaction, such as P_2O_5 and H_3PO_4, to form stable phosphates.

While there have been a number of catalytic degradation studies done on DMMP, the number of studies on MPA degradation is more limited. Davies *et al* studied the decomposition of MPA on the Al(111) surface and found that the P-C bond was stable to temperatures up to 570°C.[33] Other studies involve the use of oxidation methods [29] or the use of biological catalysts such as E.coli bacterium.[30;31]

Earlier research at Murdoch University focused on the degradation of DMMP using iron powder.[3] In that project the reaction was performed in a simple reflux system at *ca.* 180°C and a white powder resulted which was found to contain the Fe(II) and Fe(III) salts of methyl methylphosphonate (MMP). This white powder was found to degrade at *ca.* 300°C to a material that was unidentified, but thought to be an iron phosphate species. Minor degradation products detected and identified included CH_3OH, CH_4 and CO_2.

As stated earlier, this study aims to investigate the catalytic degradation of MPA using iron oxide, iron phosphate and iron powder, as well as aluminium/aluminium oxide. MPA is used in this study because it is the final hydrolysis product of many nerve agents, and observation of the formation of carbon-containing gases indicates P-C bond cleavage, which has previously proven difficult to achieve.[23;33] The main analytical method used is temperature programmed EGA-FTIR.

3. Experimental

3.1 Reagents

The reagents in this study were used as supplied without further treatment. MPA was purchased from Aldrich Chemicals and quoted to be 98% pure. Iron powder was purchased from Ajax Chemicals. This powder (used in the Honours project) was determined to be *ca*. 90% pure by energy dispersive spectroscopy (EDS) analysis. Iron (III) phosphate ($FePO_4$) was purchased from Merck Chemicals and quoted with max. 0.001% SO_4. The iron (III) oxide (Fe_2O_3, pigment grade), aluminium pans, inert pans and the aluminium oxide powder were obtained from the laboratories at DSTO.

3.2 Sample preparation

For MPA alone, *ca*. 100 mg, was ground for *ca*. 1 min in a crucible with a glass pestle and subsequently a small aliquot of this, *ca*. 10 mg, was taken for EGA-FTIR.

For Fe/MPA, Fe_2O_3/MPA, $FePO_4$/MPA and Al_2O_3/MPA, 1:1 molar ratios of mixtures were placed in a crucible and ground with a glass pestle for *ca*. 1 min under atmospheric conditions. The total sample weight was between 100-500 mg. A small aliquot, *ca*. 20-30 mg, of this sample was then taken for EGA-FTIR.

Evolved gas analysis - Fourier transform infrared spectroscopy – Small aliquots of MPA and the mixtures were weighed in an inert or aluminium reaction vessel and placed in a small tube furnace (internal diameter ≈ 10mm). A slightly larger tube furnace and sample tube was used for the experiments with the inert vessels.
 The mixture was heated at 10°C/min from ambient to 650°C under a gaseous atmosphere (nitrogen, air or oxygen), flowing at approximately 50 ml/min. The flow rate was calibrated for air and would vary slightly for the other gases due to differences in density. The evolution profiles were corrected for this difference in flow rate. If gas evolution was still occurring when the temperature reached 650°C, the furnace was held at 650°C until no further gas evolution was observed. The gases evolved from the samples were continuously passed through a 10 cm x 1 cm (internal dimensions) gas cell mounted in the cell compartment of a Bruker IFS88 FTIR spectrometer (Figure 2). The cell and transfer lines (1.5 mm PTFE) were operated at room temperature. Spectra were recorded at 2 scans per second with 4 cm^{-1} resolution. A total of 25 scans were averaged into a single spectrum, which represents a 2°C change in temperature. A background spectrum was recorded just prior to the start of the experiment (when no gases were evolved) and automatically subtracted by the software to give absorbance spectra. Post run processing of the data was performed to give stack plots and evolution profiles for the individual decomposition species. Experiments conducted in aluminium pans were performed using a small tube furnace.
The parameters for the evolution profiles were as follows (Table 1): For CO_2, the absorbance peak height at 2360cm^{-1} was measured relative to a baseline point at 2400 cm^{-1}. For H_2O, the absorbance peak height at 1652.7cm^{-1} was measured relative to a baseline point at 1656.8cm^{-1}. For CO, the peak height at 2116 cm^{-1} was measured relative to a baseline point at 2143 cm^{-1}. For CH_4, the area of the absorbance peak at 3016 cm^{-1} was measured relative a linear baseline between 3023.97 and 3003.16 cm^{-1}. For CH_2O, the area of the absorbance peak between 2842 and 2592 cm^{-1} was measured relative to a

linear baseline between 3237 and 2527 cm^{-1}. The intensity of this evolution profile was divided by a factor of 10 for comparability with the other profiles.

The evolution profiles were all normalised to a weight of 10mg MPA being present in the sample aliquots so that the results from different catalysts could be directly compared.

Table 1 - Infrared measurement parameters

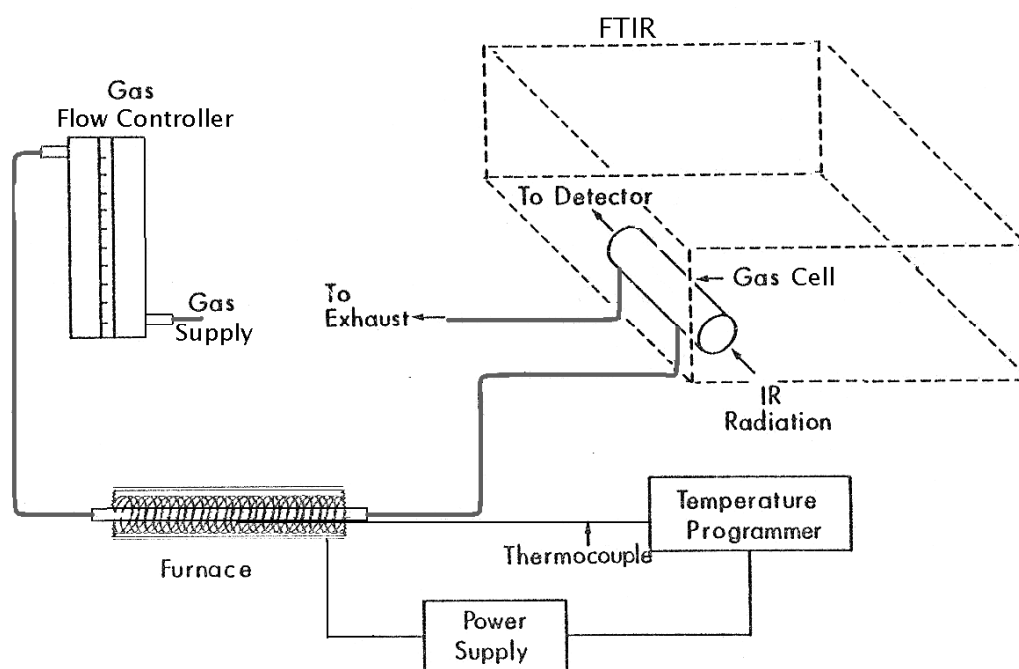| Peak	Peak Position (cm^{-1})	Baseline Point (cm^{-1})
CO_2	2360	2400
H_2O	1652.7	1656.8
CO	2116	2143
CH_4*	3016	3023.97 – 3003.16
CH_2O*	2842 - 2592	3237 - 2527

- Peak area measured instead of peak height

Figure 2 – Schematic of EGA-FTIR apparatus

4. Results

Evolved gas analysis - Fourier transform infrared spectroscopy (EGA-FTIR) was performed on a number of samples of MPA, Fe/MPA, Fe_2O_3/MPA, $FePO_4$/MPA and Al/Al_2O_3/MPA under nitrogen, air and oxygen atmospheres. Most of the gases evolved in the samples contained carbon, indicating that the P-C bond in the MPA was cleaved during the process. Similar experiments on the catalysts alone gave only trace amounts of evolved gases. Water was observed in some samples in the temperature range 100-300°C. This is thought to be water of hydration of MPA or due to salt formation at lower temperatures (i.e. acid + base → salt + water). It should also be noted that MPA melts at 105 – 107°C hence, in the absence of catalyst, it will spread uniformly over the pan.

Based on our preliminary assessment no phosphorus-containing gases are evolved in any of the experiments. However, at high temperatures in some experiments using the smaller furnace, the spectra were superimposed on a sloping baseline that was more pronounced in the higher frequency region. This baseline shift is due to scattering caused by the presence of aerosols.[32] Absorbances in the lower region of the infrared spectrum (*ca*. 750-1250 cm^{-1}) were observed. This is probably due to an aerosol containing phosphorus-oxygen species but further investigation is required.

The temperature range over which the gases were evolved and the shape of the evolution profiles are discussed for individual samples below.

4.1 Degradation of MPA in an Inert Pan

Temperature-programmed EGA-FTIR was performed on crushed samples of MPA in an inert pan under nitrogen, air and oxygen atmospheres (Figure 3). The total quantity of evolved gases was relatively small (IR maximum absorbance of *ca*. 0.08 arbitrary units) compared with subsequent experiments (which typically had IR maximum absorbances of *ca*. 0.3 – 1.0 arbitrary units). The temperature measurements are estimated to be correct to +/- 5°C.

Temperature ranges over which gases evolved were 540-650°C in nitrogen, 425-650°C in air and 225-650°C in oxygen. The evolved gases included CH_2O, CO_2, CH_4 and H_2O, except under nitrogen where only CH_4 was detected. At the conclusion of the temperature-programmed experiment, there were small amounts (too small to be collected effectively) of black char observed, which was not identified. Also, a liquid condensate had collected in the cool section of the sample tube, probably indicating that most of the MPA had distilled from the sample pan.
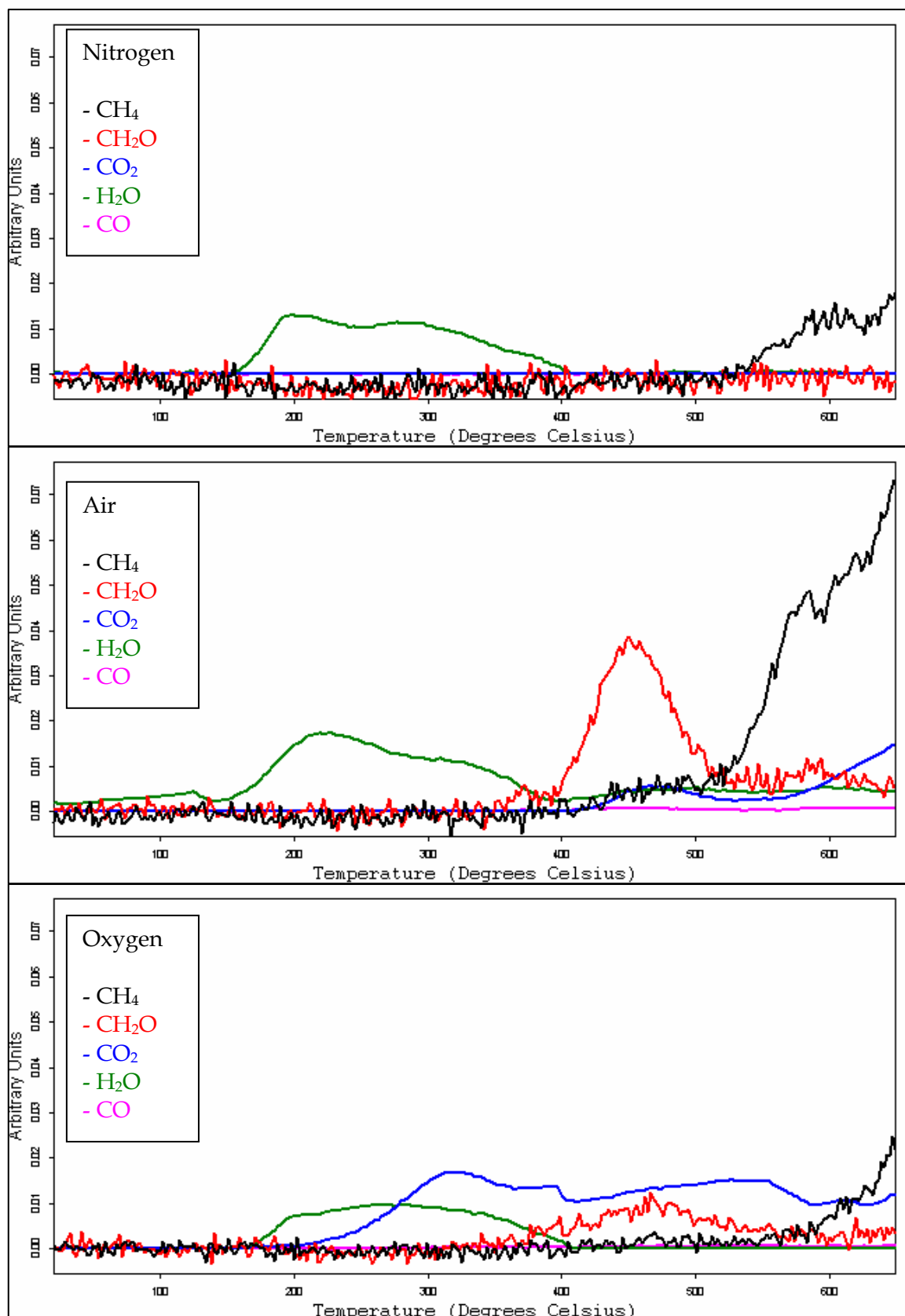
Figure 3 – EGA-FTIR evolved gas profile of MPA in an inert pan under nitrogen, air and oxygen

4.2 Degradation of MPA-Fe Powder

Temperature-programmed EGA-FTIR was performed on crushed samples of Fe/MPA in an inert pan under nitrogen, air and oxygen atmospheres. There was a relatively large amount of evolved gases (Figure 4) compared with MPA in the absence of Fe powder (Figure 3).

Temperature ranges over which gases evolved were 450-650°C in nitrogen, 425-650°C in air and 400-650°C in oxygen. The evolved gases contained CH_2O, CO_2, CH_4, CO and H_2O, except under nitrogen where no CO was detected. In all cases a large (mass basis) quantity of residue remained. This residue obtained from the experiment run under air was analysed by transmission FTIR (KBr discs). Observed absorbances (Appendix 1) in the region 900cm^{-1} – 1300cm^{-1} suggest the presence of a phosphorus-oxygen species.[34]

Apart from water at ~200°C, formaldehyde was the first gas detected in each case. Some evolution was observed at a lower temperature (375°C) in air, although the amount was minimal. The amount of oxygen-containing gases generally increased with amount of oxygen present in the atmosphere, usually with a corresponding decrease in the amount of methane detected. In each of the Fe:MPA 1:1 experiments in the different atmospheres, a small amount of condensate collected in the cool end of the sample tube. This condensate was not identified.
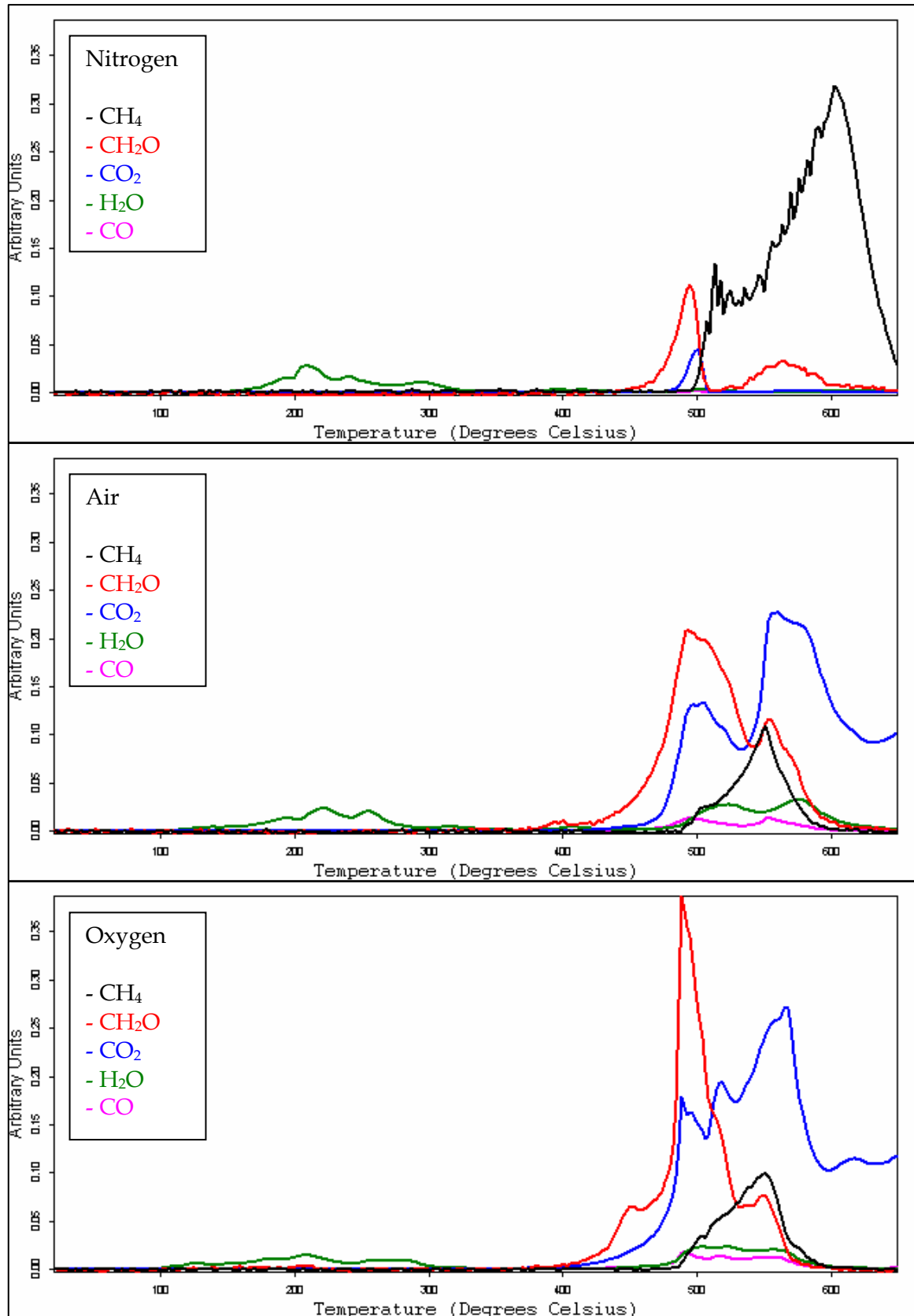
Figure 4 – Fe/MPA evolved gas traces for nitrogen, air and oxygen

4.3 Degradation of MPA-Fe$_2$O$_3$ powder

Temperature-programmed EGA-FTIR was performed on crushed samples of Fe$_2$O$_3$/MPA in an inert pan under nitrogen, air and oxygen atmospheres (Figure 5). The quantities of gases evolved were greater than for similar experiments carried out with MPA alone (Figure 3).

Under all atmospheres the temperature range over which gas evolved was 375-650°C. The evolved gases contained CH$_2$O, CO$_2$, CH$_4$, CO and H$_2$O, except in an oxygen atmosphere where negligible amounts of CH$_4$ were detected. In all cases a large (mass basis) quantity of residue remained.

Carbon dioxide was generally the first gas to be observed. The gas evolution peak due to the formation of carbon dioxide was always observed just before the gas evolution peak due to formaldehyde. Generally, more oxygen containing gases were formed as the amount of oxygen in the atmosphere increased, with a corresponding decrease in the amount of methane. In the oxygen atmosphere negligible amounts of methane were formed, while significant quantities were formed in air and nitrogen.

For the experiment run in an air atmosphere the remaining residue was analysed by FTIR (Appendix 2), and absorption bands at 967, 1025 and 1089 cm^{-1} suggest some of the residue contains an iron phosphate species. An infrared spectrum of FePO$_4$ was run and a broad peak was observed at 1030 cm^{-1}, with shoulders at 1058 and *ca*. 1080 cm^{-1}. A broad band in the region 500 – 600 cm^{-1} may indicate the presence of unreacted iron oxide.
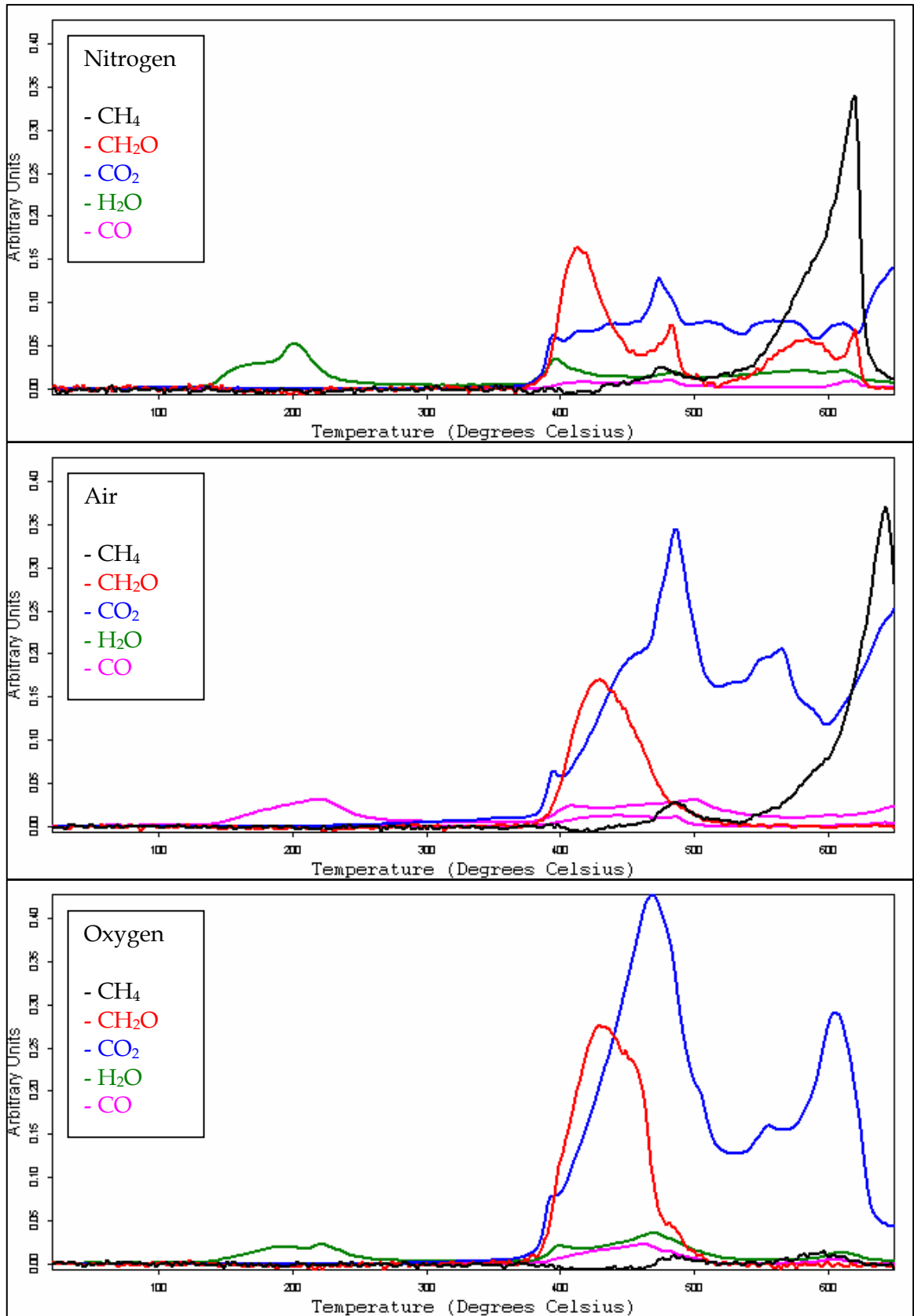
Figure 5 – Fe$_2$O$_3$/MPA evolved gas traces for nitrogen, air and oxygen

4.4 Re-usability of catalyst

Preliminary duplicate experiments with the residue obtained from the reaction of Fe_2O_3/MPA (2:1) in an oxygen atmosphere showed that the residue was capable of catalysing subsequent reactions for at least one more run. In these experiments (Figure 6), the residue from the first experiment was mixed in a 2:1 mole ratio with MPA (assuming that the residue was primarily Fe_2O_3) in an aluminium pan and another EGA-FTIR analysis performed. A large peak in the CO_2 profile was observed at *ca*. 450°C in the first experiment (true peak height calculated based on weaker peaks because the main peak due to CO_2 exceeded the dynamic range of the instrument *ca*. 6 absorbance units).

Gas evolution was observed over temperature ranges of 400-650°C in each case. The amount of CO_2 formed in the second case appears to be less than in the first, with corresponding increases in methane formation and to a lesser extent formaldehyde. Higher temperature carbon dioxide evolution is also observed but this occurs over a greater temperature range.

Although the amount of carbon dioxide appears to be less in the second case, the same gas evolution profile is observed. This profile is not seen in the 1:1 molar ratio Fe_2O_3:MPA experiments in an aluminium pan. The narrow temperature range over which CO_2, CH_4 and CO forms is an unusual observation and warrants further investigation, however, it is clear that the amount of catalyst present affects the reaction profile of MPA in the presence of Fe_2O_3.
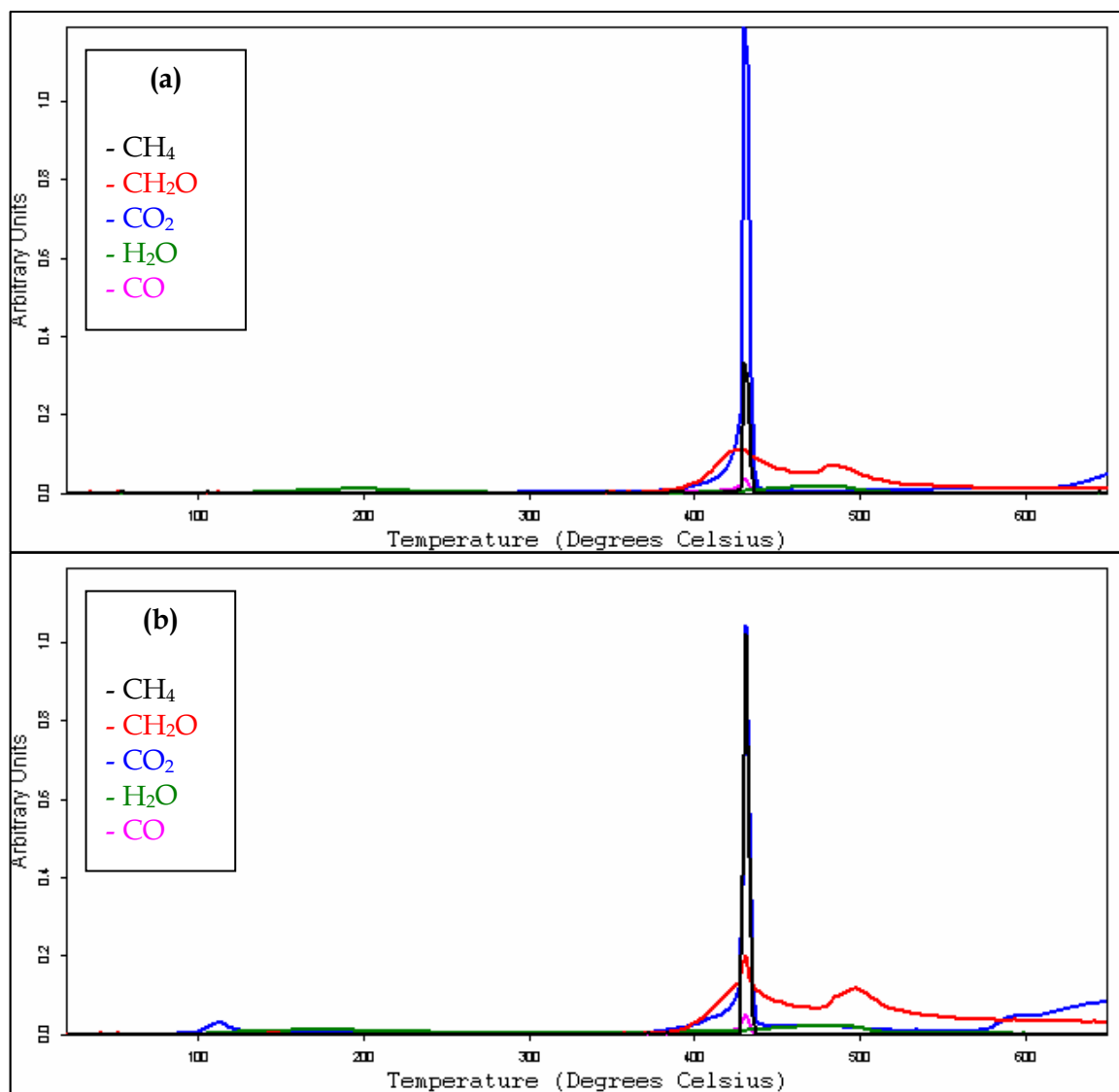
Figure 6 – EGA-FTIR evolved gas profile of 2:1 molar ratio of (a) Fe_2O_3:MPA (b) spent catalyst (used once previously):MPA in oxygen

4.5 Degradation of MPA-FePO₄ powder

Temperature programmed EGA-FTIR was performed on crushed samples of $FePO_4$/MPA in an inert pan under nitrogen, air and oxygen atmospheres (Figure 7). The quantities of evolved gases were greater than for MPA alone in an inert pan (Figure 3).

Under all atmospheres gases were formed in the temperature range of 400-650°C. The evolved gases contained CH_2O, CO_2, CH_4, for nitrogen, air and oxygen. Under the oxygen atmosphere CO and H_2O were also detected. In all cases a large (mass basis) quantity of residue remained.

Formaldehyde was the first carbon containing gas detected in each case. The evolution of carbon dioxide followed the evolution of formaldehyde under all atmospheres, with the evolution profiles appearing very similar. Under the oxygen atmosphere, the evolution profiles of formaldehyde, carbon dioxide and methane appear very similar. This suggests that the formation of these gases may be related, but further investigation is required to elucidate the mechanisms involved. Generally, more oxygen containing gases were formed as the amount of oxygen in the atmosphere increased, with a corresponding decrease in the amount of methane.
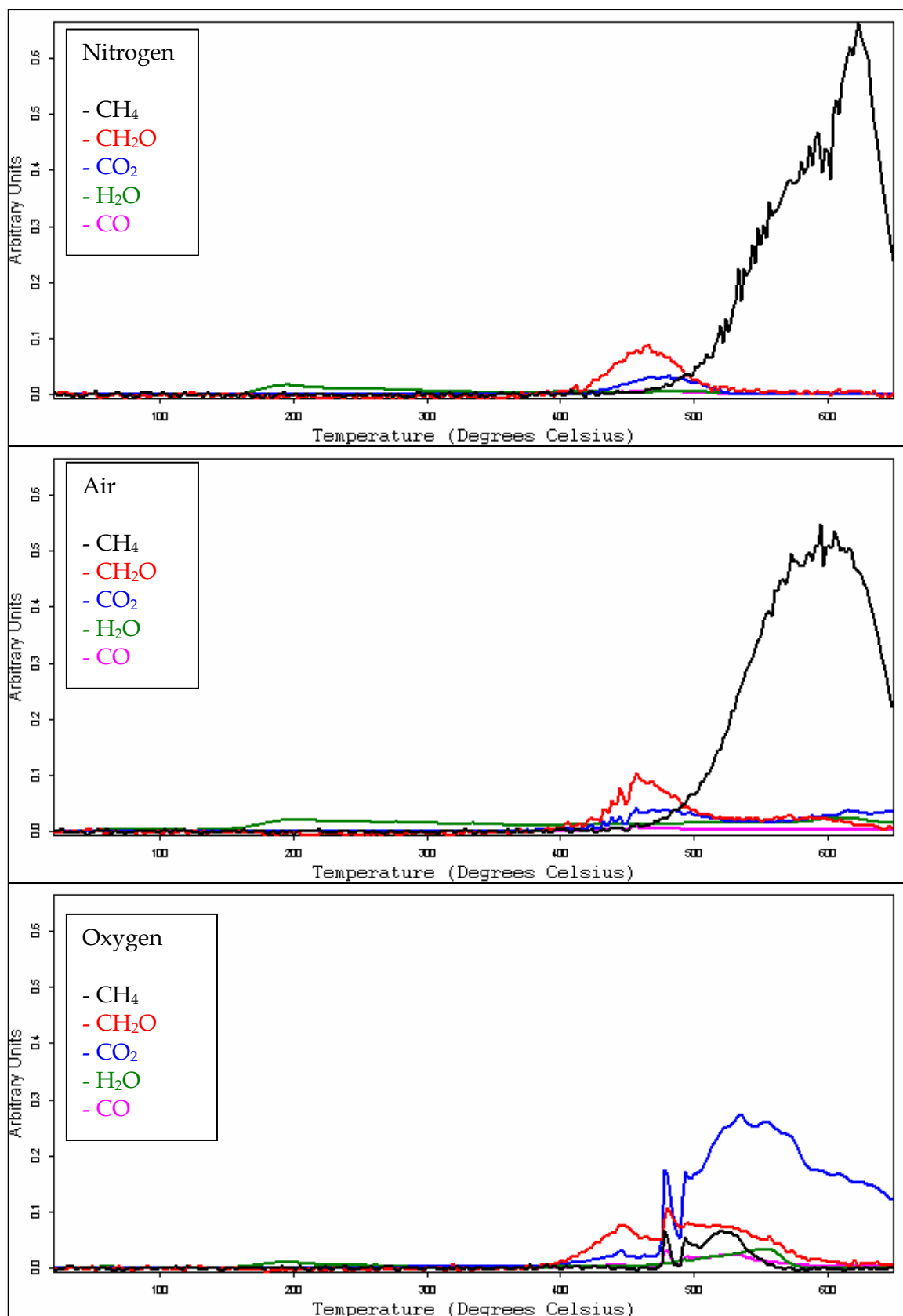
Figure 7 – EGA-FTIR evolved gas profile of FePO₄/MPA for nitrogen, air and oxygen

4.6 Degradation of MPA in an Al Pan

(NB. MPA melts at 105 – 107°C, spreads over surface of Al pan, which contains Al_2O_3. Therefore, the different results observed in an inert pan and Al pan may be due to the influence of Al and/or a surface coating of Al_2O_3).

Temperature programmed EGA-FTIR was performed on crushed samples of MPA in an aluminium pan under nitrogen, air and oxygen atmospheres (Figure 8). There were relatively large amounts of evolved gases compared with MPA in an inert pan.

Temperature ranges over which gases evolved were 525-650°C in nitrogen, 510-650°C in air and 490-650°C in oxygen. The evolved gases included CH_2O, CO_2, CH_4, CO and H_2O, except under nitrogen where only CH_4 was detected. Infrared absorptions in the lower frequency part of the spectrum (most intense peak at *ca*. 995 cm^{-1}) may indicate the evolution of phosphorus-oxygen containing species. These are likely to be aerosols rather than gaseous species because the spectra were superimposed on sloping baseline, which is usually observed when aerosols are detected due to scattering.[32] In all cases a small quantity of residue remained and infrared spectroscopic analysis showed a major peak at *ca*. 1250cm^{-1}, possibly aluminium metaphosphate.[34]

Under nitrogen, methane was the only carbon containing gas that was detected. Under air and oxygen, formaldehyde was detected first and in these two cases the first gas evolution peaks for CH_2O, CO_2, CH_4 and CO all occur at the same temperature. Methane was the predominant gas species in each case and in the air and oxygen cases it appears to form in two distinct processes. As the amount of oxygen in the atmosphere increased, the amount of oxygen-containing gases detected increased.
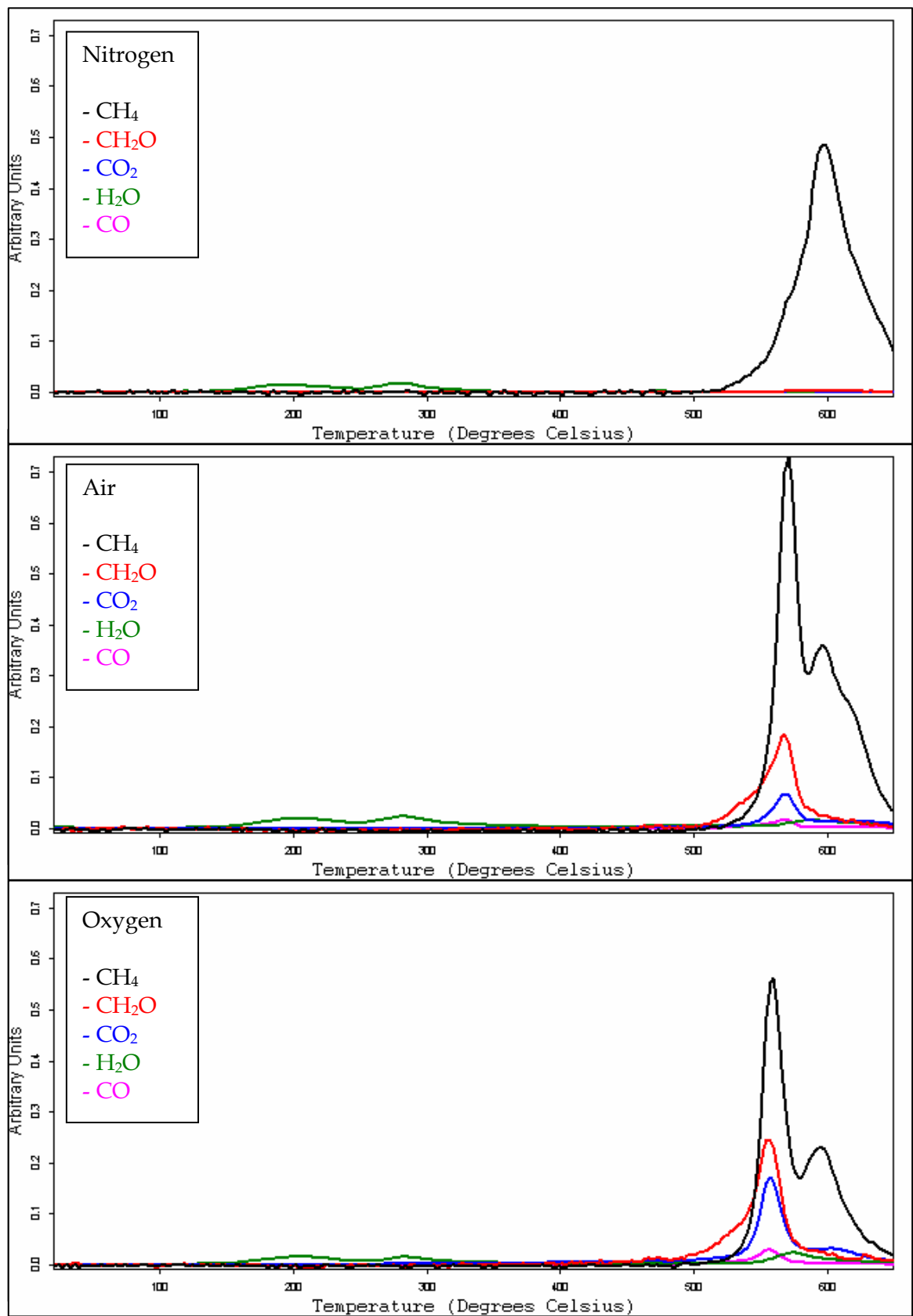
Figure 8 – EGA-FTIR evolved gas profile of MPA in an Al pan under nitrogen, air and oxygen

4.7 Catalyst regeneration experiments

The following study was undertaken to determine the possibility of regenerating iron, ferric oxide and ferric phosphate catalysts. The evolution profiles have been normalised for each experiment, i.e. quantitative comparison is valid between experiments using the same catalyst but not between experiments using different catalysts.

a) Fe_2O_3

A 1:1 molar ratio of Fe_2O_3:MPA was subjected to temperature programmed EGA-FTIR. Subsequently, the residue was mixed with MPA in a 1:1 ratio (assuming the residue consisted primarily of Fe_2O_3 i.e. total consumption/decomposition of MPA) and subjected to the same experiment. The residue from the second experiment was then divided into two parts, with one of these portions being regenerated by heating to 1000°C for 30 minutes, to burn off all organics, and the second portion left untreated. Both of these portion were then mixed with MPA in a 1:1 molar ratio (again assuming the residue is primarily Fe_2O_3) and subjected to temperature programmed EGA-FTIR. The corresponding evolution profiles are presented below (Figure 9).

Gases evolved over temperature ranges of 410-650°C with regeneration and 415-650°C without regeneration. The gases evolved included CH_2O, CO_2, CO, CH_4 and H_2O. More methane and formaldehyde appeared to be formed in the case of regeneration. However, the temperature of evolution of carbon dioxide was lower in the case of no regeneration. Also, the gases evolved from the regenerated catalyst experiment had a different evolution profile to those of the initial run.

One possible explanation for these observations is that the Fe_2O_3 is reacting with the MPA to form $FePO_4$, and this is catalysing the reaction. To test this hypothesis, a sample of 1:1 $FePO_4$:MPA was subjected to EGA-FTIR under air. The evolution profile appeared similar to the regenerated Fe_2O_3 experiment. This is evidence that the species being regenerated is an iron phosphate species, but detailed residue analysis is needed to confirm this.

b) $FePO_4$

Regeneration of the iron phosphate catalyst was also attempted. As with the iron oxide, a 1:1 ratio of $FePO_4$:MPA was subjected to two EGA-FTIR runs, with the residue of the first being used in the second experiment. The residue of the second experiment was then divided into two parts. One of these was subjected to EGA-FTIR with MPA in a 1:1 molar ratio (assuming the catalyst was predominantly $FePO_4$) without treatment. The other portion was subject to regeneration at 1000°C for 30 minutes (Figure 10). While the non-regenerated catalyst showed no activity the regenerated catalyst showed significant activity, with methane producing the largest evolution profile. This profile appears similar to the original $FePO_4$/MPA experiment suggesting the regenerated catalyst contains $FePO_4$. The methane evolution from regenerated $FePO_4$/MPA and to a lesser extent Fe_2O_3/MPA shows a series of spikes superimposed on top of the evolution profiles. These spikes correspond to the rapid formation of methane and clearly show catalytic activity. This behaviour is also shown on some of the other evolution profiles.

The residue from this experiment was regenerated once more at 1000°C for 30 minutes. Transmission FTIR (KBr disc) was performed on this regenerated catalyst and compared to the spectrum of $FePO_4$ (Appendix 3). Absorbance peaks were observed at 967, 1033 and 1080cm^{-1} in the regenerated catalyst, possibly suggesting an iron phosphate species.

Also, an absorbance band was observed at $1229cm^{-1}$, suggesting another phosphate species that may aid in MPA degradation is present. The non-regenerated residues were also studied by transmission FTIR spectroscopy and were found to containadditional peaks at 1269 and $1320cm^{-1}$. The species from which these peaks arise are thought to be responsible for catalyst poisoning.

c) Fe

In light of the above results an attempt was made to regenerate the iron catalyst. As in the above examples, a 1:1 ratio of Fe:MPA was subjected to two EGA-FTIR experiments, with the residue of the first being used in the second experiment. The residue of the second experiment was then divided into two parts with one subjected to EGA-FTIR with MPA in a 1:1 molar ratio (assuming the catalyst was predominantly Fe) without treatment. The other portion was subject to regeneration at 1000°C for 30 minutes (Figure 11). As with the iron phosphate catalyst, there was decomposition on both regenerated and non-regenerated catalyst, with the regenerated species showing more activity. Methane was the major product in both cases. These profiles appear similar to the Fe_2O_3:MPA case, with the regenerated species showing more activity than the non-regenerated species.

It appears from the evolution profiles that regeneration enhances the catalytic effect of the spent catalyst. More analysis is needed to identify the surface species present and determine the changes that occur upon regeneration. The evolution profile of the regenerated catalyst appears similar to the $FePO_4$/MPA, suggesting that iron phosphate may be present after regeneration. Some CO_2 is observed at lower temperatures (represented by small spikes in the evolution gas profile) in the case of non-regeneration of the iron oxide catalyst and the cause of this evolution and its reproducibility are also further areas of potential study. The near complete restoration of the iron phosphate catalyst is also significant and further study could result in its use as a catalyst for chemical agent degradation.

The evolution profiles from the first cycle in the Fe/MPA regeneration experiment are different from those for air in Figure 4. This is because the experiment had to be scaled up to provide enough catalyst for the regeneration experiments. The Fe/MPA mixture foamed during the experiment probably restricting the migration of air to within the sample. The decomposition gases evolved show less oxygenated species, which supports this idea.
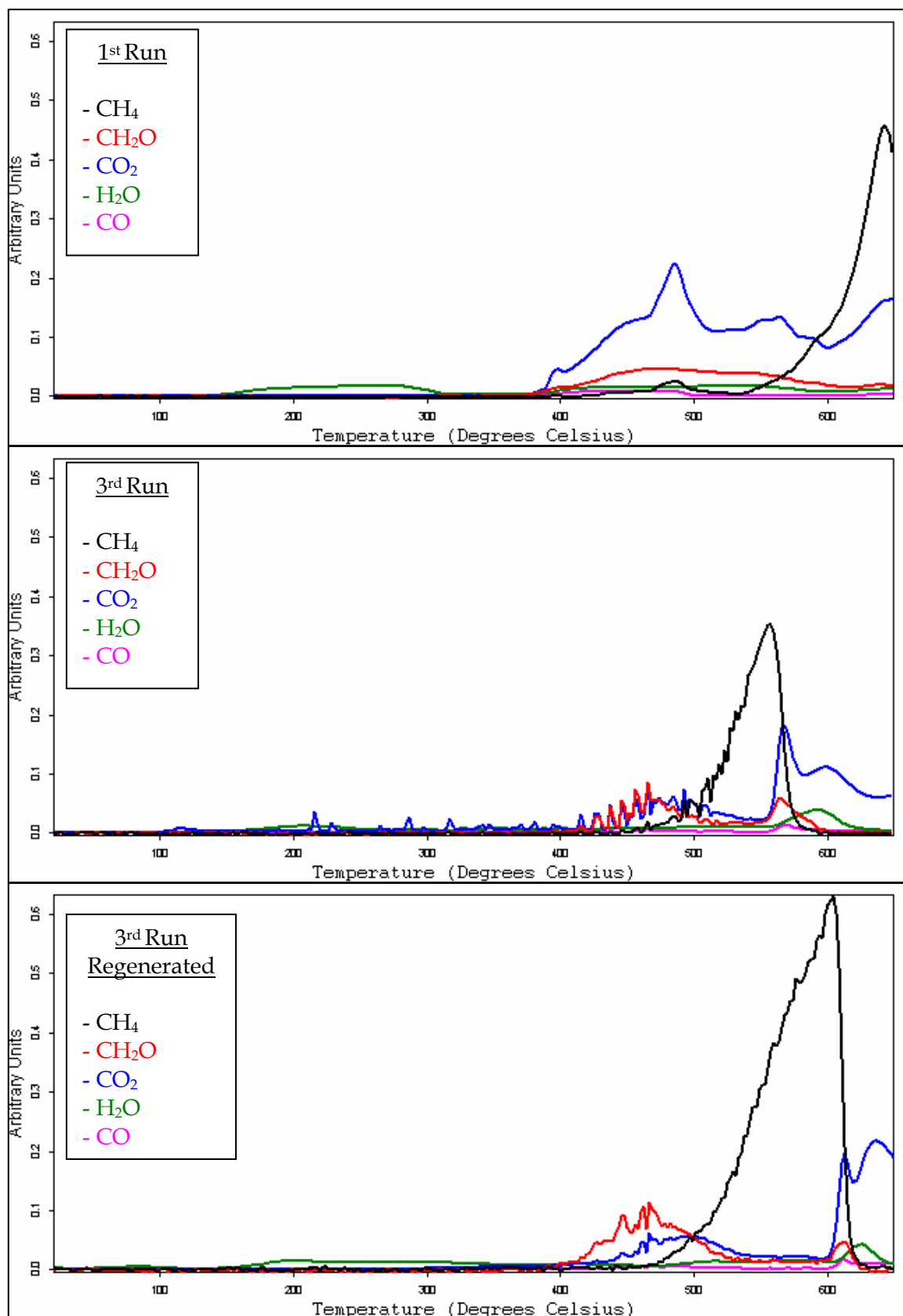
Figure 9 – FTIR-EGA evolved gas profiles from Fe₂O₃/MPA regeneration experiments in air
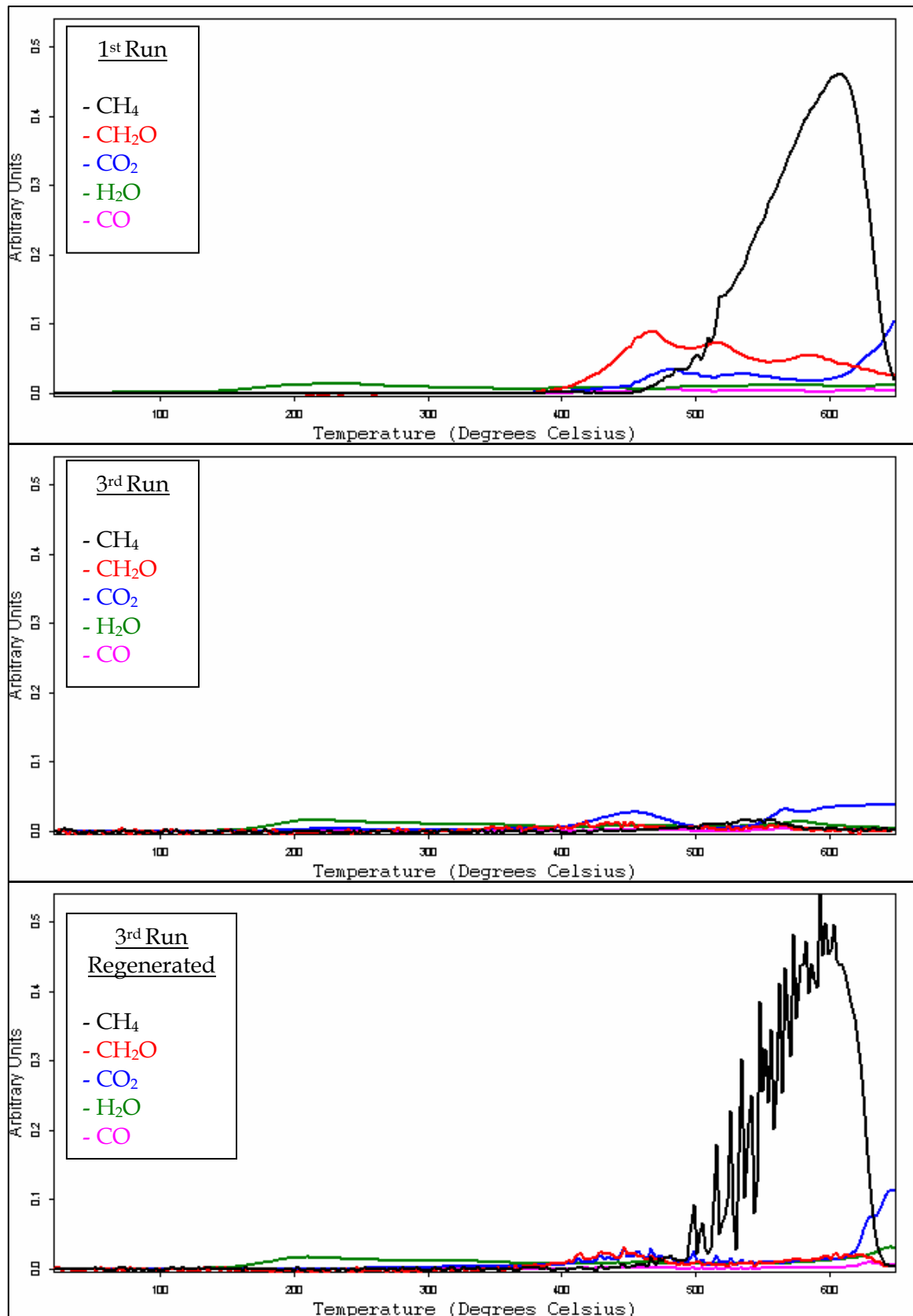
Figure 10 – FTIR-EGA evolved gas profiles for FePO$_4$/MPA regeneration experiments in air
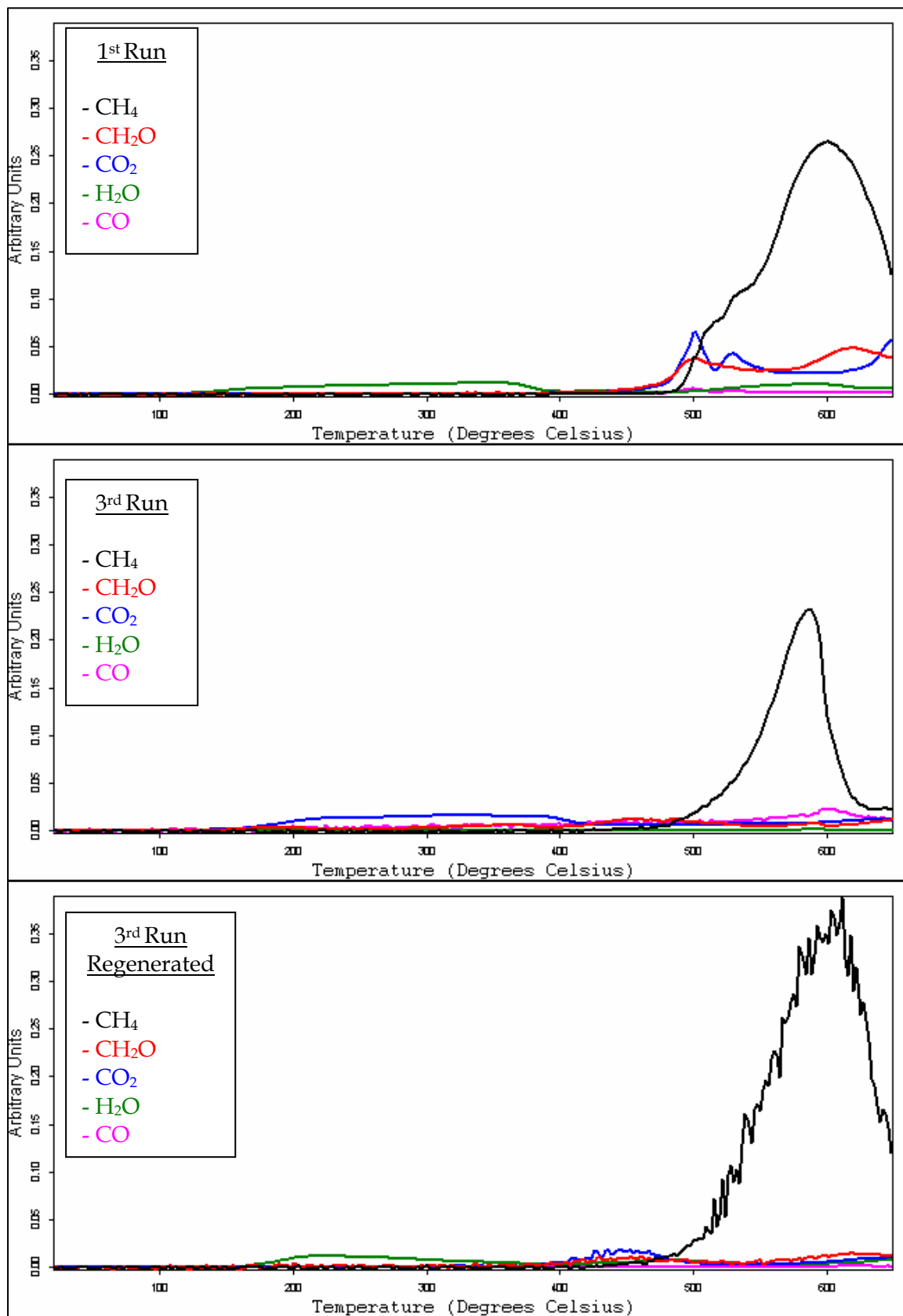
Figure 11 – FTIR-EGA evolved gas profiles for Fe/MPA regeneration experiments in air

5. Discussion

All the experiments involving MPA with catalyst produced significant concentrations of decomposition gases with only small amounts of condensate forming in the apparatus. In the experiments with no catalyst in an inert pan, most of the MPA distilled from the pan and condensed in a cool section of the tube. Also, only a very low concentration of decomposition gases were evolved and char formed in and around the reaction vessel. This gives some insight into the role that the catalyst performs in immobilising the MPA for subsequent degradation. It suggests that all the catalysts and metallic pans react with MPA to form salts. This reaction probably at least partially explains the low temperature evolution of water during these experiments.

The experiments with Fe/MPA in an inert pan showed the evolution of significant amounts of gases beginning at temperatures of 400-450°C. The gas evolution is minimal until *ca*. 450°C when there is a rapid increase in evolution of formaldehyde. In contrast to these experiments, Fe_2O_3/MPA experiments in an inert pan show a rapid rate of evolution of gases initially, which begin at a lower temperature (375°C). This may indicate that Fe_2O_3 is a better catalyst than Fe. $FePO_4$ was also demonstrated to have ability to catalyse the degradation of MPA.

Experiments in which MPA was decomposed in an Al pan was shown to have considerably less catalyst activity than the iron based catalysts, because the evolution of carbon containing gaseous species only started in the 490-525°C temperature range depending on the atmosphere. Its decomposition behaviour differed from Al_2O_3(powder)/MPA in an inert pan under air (Appendix 5). Methane was the major decomposition product in both cases but the evolution peak temperature differed by 50°C. This would seem to indicate that Al plays a role in the degradation process, or that there are significant differences between a powder catalyst and a catalyst bed. Similar work by Davies *et al*. [33] shows that MPA adsorption leads to a very stable tridentate methyl phosphonate species and that the P-C bond is stable on Al/Al_2O_3 up to temperatures of 570°C.

The residue from the Fe/MPA and Fe_2O_3/MPA experiments had IR absorbance bands that were consistent with the presence of a phosphate species.[34] This may be as a result of a stoichiometric reaction with the catalyst, or may result from poisoning of the catalyst by an immobilised non-metal phosphorus species. This would not be unexpected, as some studies using iron oxide catalysts to degrade DMMP have resulted in the reaction of these catalysts with by-products, such as P_2O_5 or H_3PO_4 to form stable phosphates.[23] The effect of catalyst poisoning was shown in the regeneration experiments where the catalyst used in the third run was not regenerated. The fact that both the iron oxide and iron phosphate catalysts can be regenerated would suggest that the non-metal phosphate species have a negative impact on the degradation capability of these catalysts. The iron phosphate catalyst appeared to be the most effected by catalyst poisoning as very low concentrations of decomposition gases were detected in the third cycle (catalyst without regeneration) of the regeneration experiment. This is not unexpected as the catalyst already contains its complete set of phosphate groups, hence other phosphate species are likely to be formed.

The formation of iron phosphate species in the catalyst residue was also shown to be beneficial as iron phosphate can also catalyse the decomposition of MPA. Infrared

spectra of the residues from the used iron/iron oxide catalysts in Appendix 4 show the presence of phosphate absorptions. Also, the evolution profiles for the regenerated catalysts were all similar and methane was the most intense evolution profile. These methane evolution profiles were also similar to that of the initial cycle in the $FePO_4$/MPA regeneration experiment. This is more evidence suggesting that iron phosphate is the most active species present in the regenerated catalysts. Iron phosphate is less effective as a catalyst in air than iron oxide or iron powder because less carbon-oxygen containing species were evolved at low temperatures and more methane at high temperature.

The decomposition of MPA with iron based catalysis appears to be a complex process. Only the main decomposition gases were monitored in this study. The EGA-FTIR spectra showed that other gases were also formed such as ethene and methanol. These gases have not been included in the evolution profiles because there was no clear formation behaviour across the different atmospheres. However, these gases may be important from a mechanistic point of view.

Duplicate experiments were performed for MPA alone, Fe/MPA and Fe_2O_3/MPA in a 1:1 molar ratio under air and Fe_2O_3/MPA in a 2:1 molar ratio under oxygen. In each case the profiles appeared similar and the evolution temperature of each gas was within +/- 5°C. For the purposes of this qualitative study, these were the only duplicate experiments performed. However, for accurate quantitative measurements, the reproducibility would need to be assessed after at least five experiments.

In this study, there were no measurements taken of the catalysts particle size or surface area. These measurements are important when determining the activity of the catalysts, otherwise could lead to false interpretations because of the varying surface area available for catalysis. Therefore, further experimentation is required including particle size determination to establish which catalyst has the best catalytic properties.

6. Summary and Conclusion

This study has explored the use of various metal and metal oxides for the catalytic degradation of MPA. It was found that evolution of carbon containing gases occurred at *ca*. 375°C on ferric oxide catalysts, *ca* 410°C on iron phosphate and at *ca*. 400-450°C on iron catalysts. There was greater gas evolution at lower temperatures when ferric oxide was used as a catalyst. The use of aluminium and aluminium oxide catalysts resulted in carbon containing gases being formed at *ca*. 510°C.

Fourier Transform infrared evolved gas analysis (EGA-FTIR) was shown to be a technique with great potential for use in catalytic degradation studies. The information presented in this report is only a small portion of what can be extracted from evolution profiles, which may provide detailed mechanistic information, and subsequently lead to improved catalytic degradation processes. Mechanisms have not been proposed in this report but information has been obtained that may lead to such proposals.

Preliminary attempts to regenerate the iron oxide and iron phosphate catalyst yielded favourable results. More methane appears to be formed after regeneration of the used

catalysts, which would seem to indicate that regeneration is beneficial. More experimentation is required to assess the effect of regeneration.

Further work in this study could include:

- Characterisation of the residue of the experiments to determine whether stoichiometric reaction or catalyst poisoning is occurring. This could include Inductively Coupled Plasma (ICP) analysis, X-ray Diffraction (XRD) and surface techniques such as X-Ray Photoelectron Spectroscopy (XPS).
- Investigating the regeneration of ferric oxide catalysts.
- The use of isothermal conditions at lower temperatures for longer periods of time.
- Detailed study of gas evolution profiles (including quantification of gases involved) and proposal of mechanisms, with subsequent experiments to verify these proposed mechanisms.
- Conduct experiments under helium to determine whether nitrogen is affecting the performance of the catalyst
- Assess the effect of any reactions that occur at room temperature (preliminary results indicate a difference between freshly ground samples and those left standing for some time before reaction).

The potential for the use of iron and iron oxide as a catalyst for the degradation of methylphosphonic acid has been demonstrated in the experiments conducted so far. Iron oxide was shown to be the best catalyst because of the lower temperature of gas evolution. Continued research in this area may possibly lead to catalytic degradation being used for destruction and decontamination purposes.

7. References

1) Organisation for the Prohibition of Chemical WeaponsConvention of the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction; 2000;

2) Stockholm International Peace Research Institute (SIPRI)SIPRI Yearbook 2001: Armaments, Disarmaments and International Security; Oxford University Press: 2001;

3) Moniodis, J. J. The degradation of dimethyl methylphosphonate using iron oxides / iron powder. 2001. Murdoch University. Ref Type: Thesis/Dissertation

4) Fenner, R. A. Fourier transform infrared evolved gas analysis of the thermal decomposition products of polymers. 1973. Virginia Commonwealth University. (GENERIC). Ref Type: Thesis/Dissertation

5) Davidson, R.G. Journal of Analytical and Applied Pyrolysis **1991**, 21, 181

6) de Yong, L. Environmental degradation of polytechnic magnesium powder. 2001. Melbourne University. Ref Type: Thesis/Dissertation

7) Davidson, R.G. Mikrochimica Acta **1988**, 1, 301

8) Guo, X.; Yoshinobu, J.; Yates Jr., J.T. Journal of Physical Chemisrty **1990**, 94, 6839

9) Hegde, R.I.; Greenlief, C.M.; White, J.M. Journal of Physical Chemisrty **1985**, 59, 2886

10) Smentkowski, V.S.; Hagans, P.; Yates Jr., J.T. Journal of Physical Chemisrty **1998**, 92, 6351

11) Tzou, T.Z.; Weller, S.W. Journal of Catalysis **1993**, 146, 370

12) Leslie, D. R. and Ward, J. R. Metal-ion catalysed oxidation of a G-agent simulant by oxone. 1992. Chemical Research, Development and Engineering Centre. (GENERIC). Ref Type: Report

13) Li, Y.-X.; Klabunde, K.J. Langmuir **1991**, 7, 1388

14) Li, Y.-X.; Schlup, J.R.; Klabunde, K.J. Langmuir **1991**, 7, 1394

15) O'Shea, K.E.; Beightol, S.; Garcia, I.; Aguilar, M.; Kalen, D.V.; Cooper, W.J. Journal of Photochemistry and Photobiology A - Chemistry **1997**, 107 , 221

16) O'Shea, K.E.; Garcia, I.; Aguilar, M. Res.Chem.Intermed. **1997**, 23 , 325

17) Obee, T.N.; Satyapal, S. Journal of Photochemistry and Photobiology A - Chemistry **1998**, 118, 45

18) Templeton, M.K.; Weinberg, W.H. Journal of the American Chemical Society **1985**, 107, 97

19) Templeton, M.K.; Weinberg, W.H. Journal of the American Chemical Society **1985**, 107, 774

20) Mitchell, M.B.; Sheinker, V.N.; Mintz, E.A. Journal of Physical Chemistry B **1997**, 101, 11192

21) Tesfai, T.M.; Sheinker, V.N.; Mitchell, M.B. Journal of Physical Chemistry B **1998**, 102, 7299

22)   Hegde, R.I.; White, J.M. Applied Surface Science **1987**, 28, 1

23)   Cao, L.; Segal, S.R.; Suib, S.L.; Tang, X.; Satyapal, S. Journal of Catalysis **2000**, 194, 61

24)   Henderson, M.A.; Jin, T.; White, J.M. Journal of Physical Chemisrty **1986**, 90, 4607

25)   Segal, S.R.; Suib, S.L. Chem.Mater. **1999**, 11, 1687

26)   Henderson, M.A.; White, J.M. Journal of the American Chemical Society **1988**, 110, 6939

27)   Lee, K.Y.; Houalla, M.; Hercules, D.M.; Hall, W.K. Journal of Catalysis **1994**, 145, 223

28)   Ekerdt, J.G.; Klabunde, K.J.; Shapely, J.R.; White, J.M.; Yates Jr., J.T. Journal of Physical Chemisrty **1988**, 92, 6182

29)   Bianchetta, S.; Li, L.; Gloyna, E.F. Ing.Eng.Chem.Res. **1999**, 38, 2902

30)   Cordeiro, M.L.; Pompliano, D.L.; Frost, J.W. Journal of the American Chemical Society **1986**, 108, 332

31)   Matys, S.V.; Laurinavichyus, K.S.; Nesmeyanova, M.A. Microbiology **1996**, 65, 421

32)   Davidson, R.G.; Mathys, G.I. Analytical Chemistry **1986**, 58, 837

33)   Davies, P.R.; Newton, N.G. Applied Surface Science **2001**, 181, 296

34)   Socrates, G. Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 2001, John Wiley and Sons, p290

Appendix 1: FTIR-spectra of the residue of Fe/MPA under air
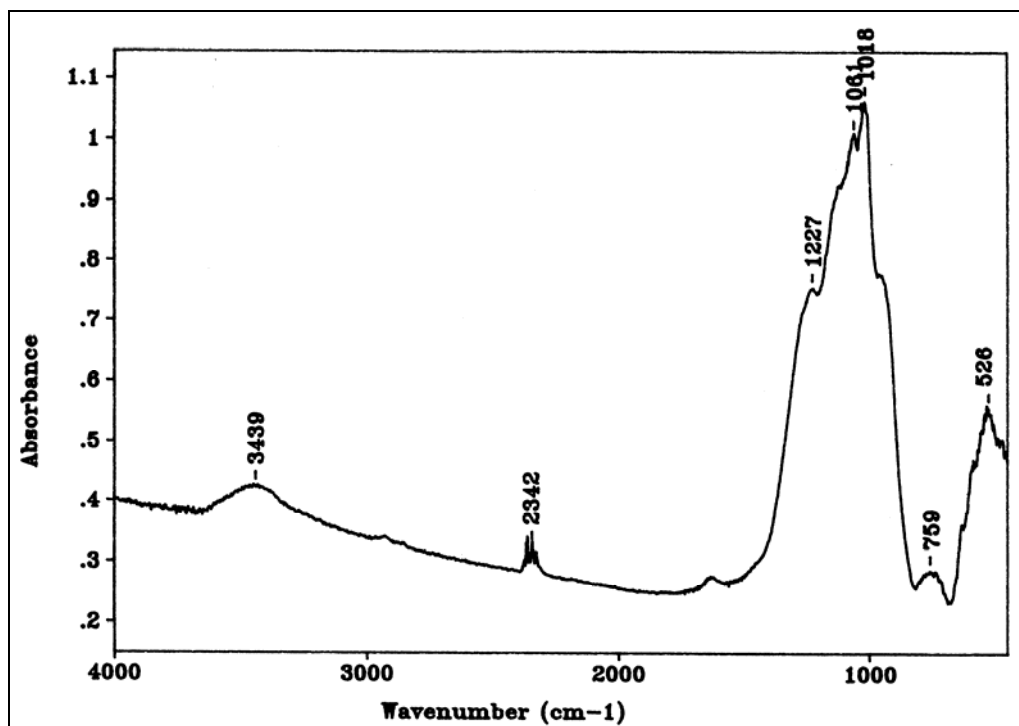
Appendix 2:   FTIR-spectra of the residue of Fe₂O₃/MPA under air
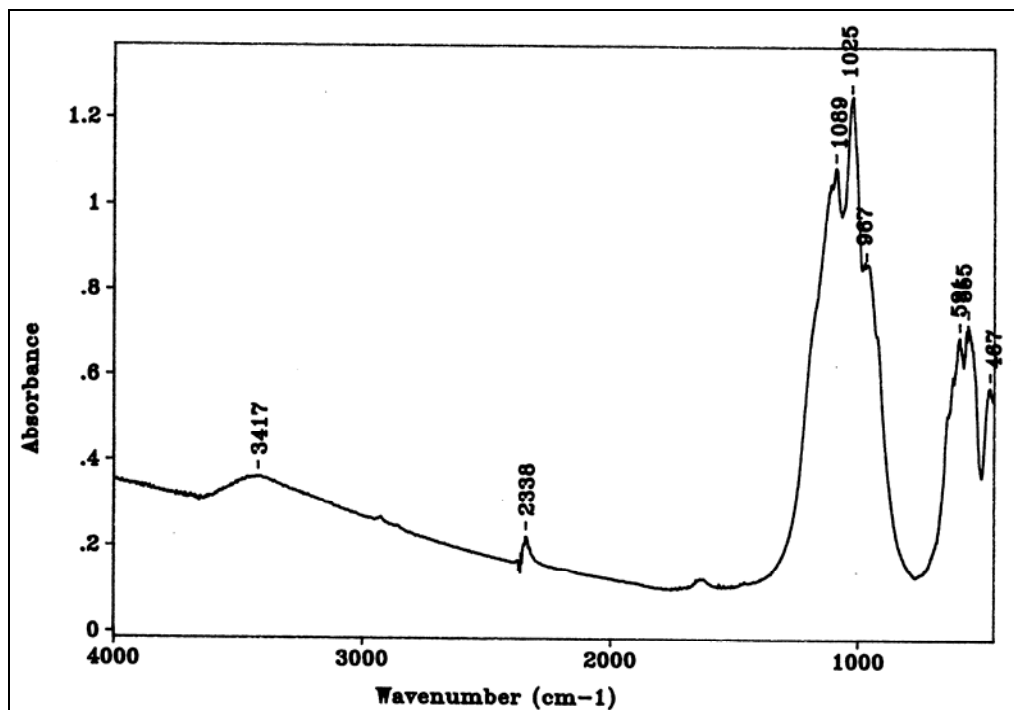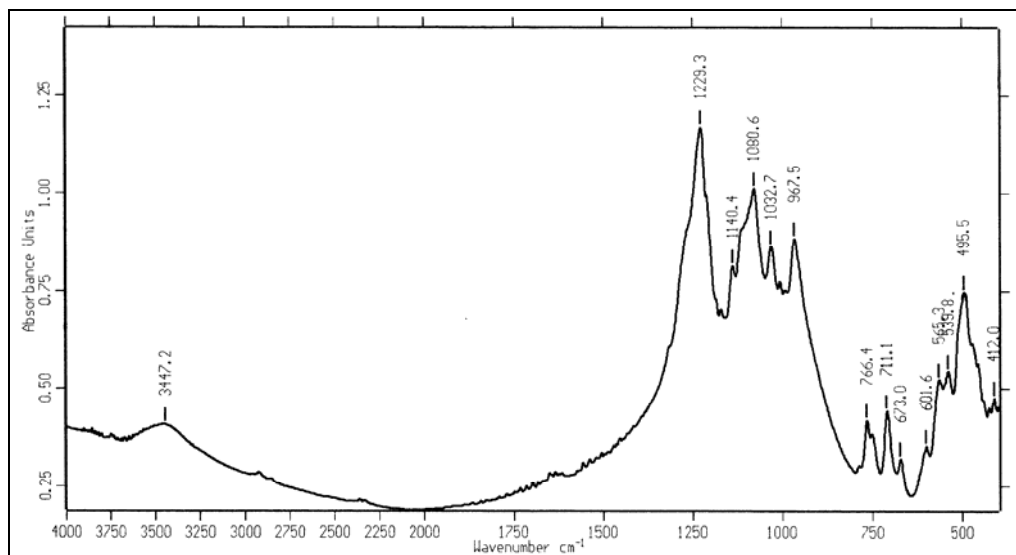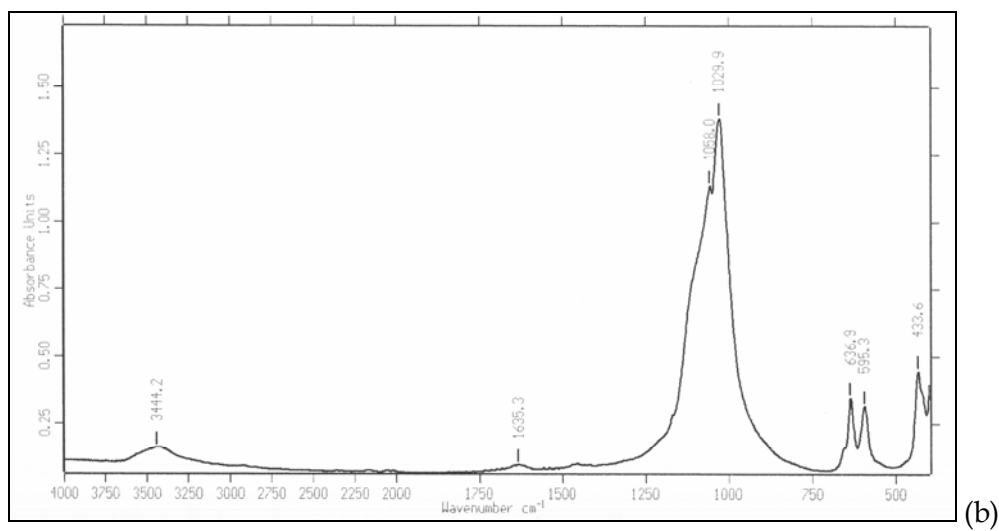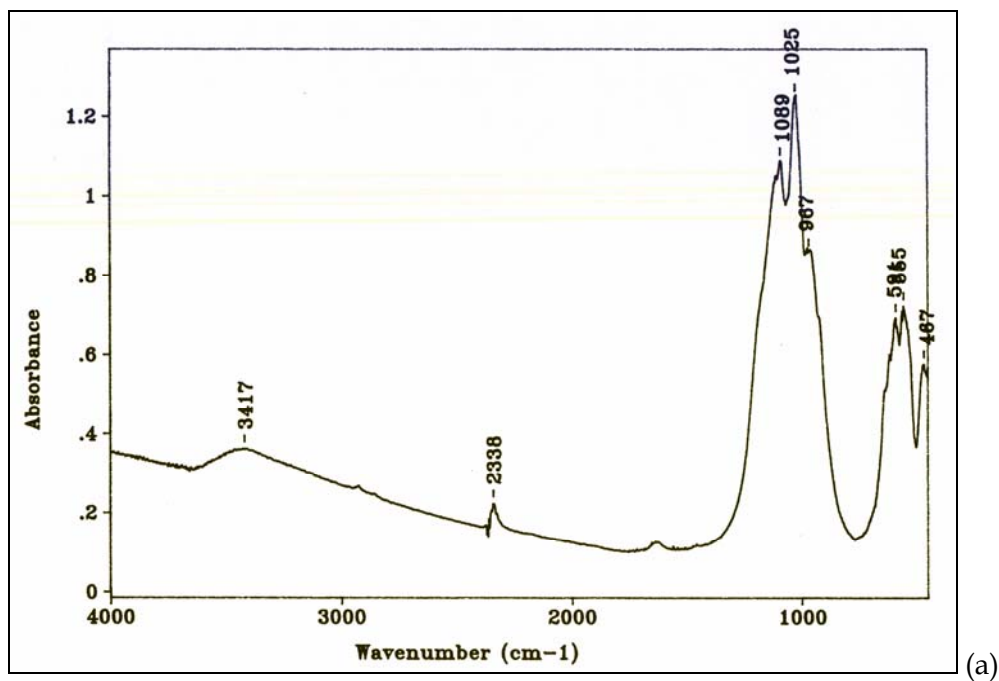
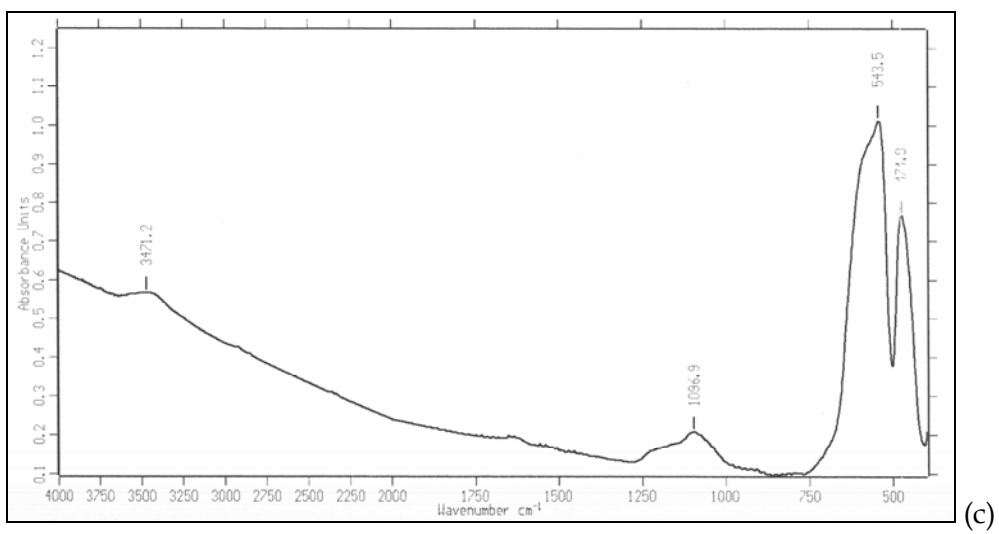# Appendix 3: FTIR-spectra of the residue of FePO$_4$/MPA under air

Appendix 4: FTIR spectra of the residue of Fe_2O_3/MPA run in air (a), $FePO_4$ (b) and Fe_2O_3 (c)

(a)

(b)

(c)

36

Appendix 5: EGA-FTIR evolved gas profile of Al₂O₃/MPA in an inert pan under air (top) and MPA in an Al pan (assumed to have a surface layer of aluminium oxide) under air (bottom)
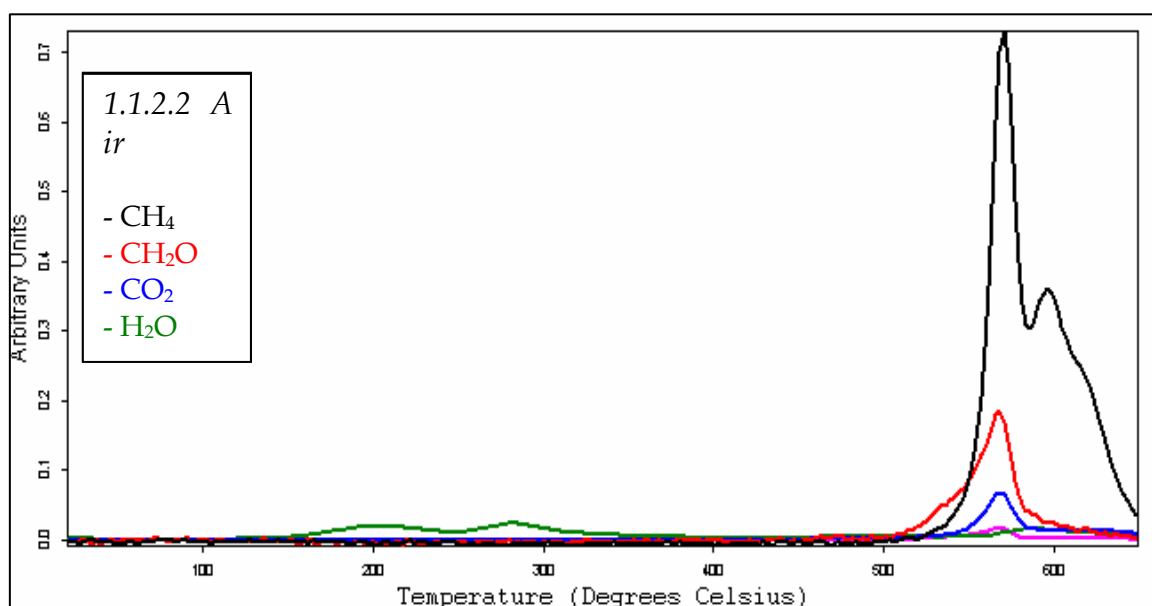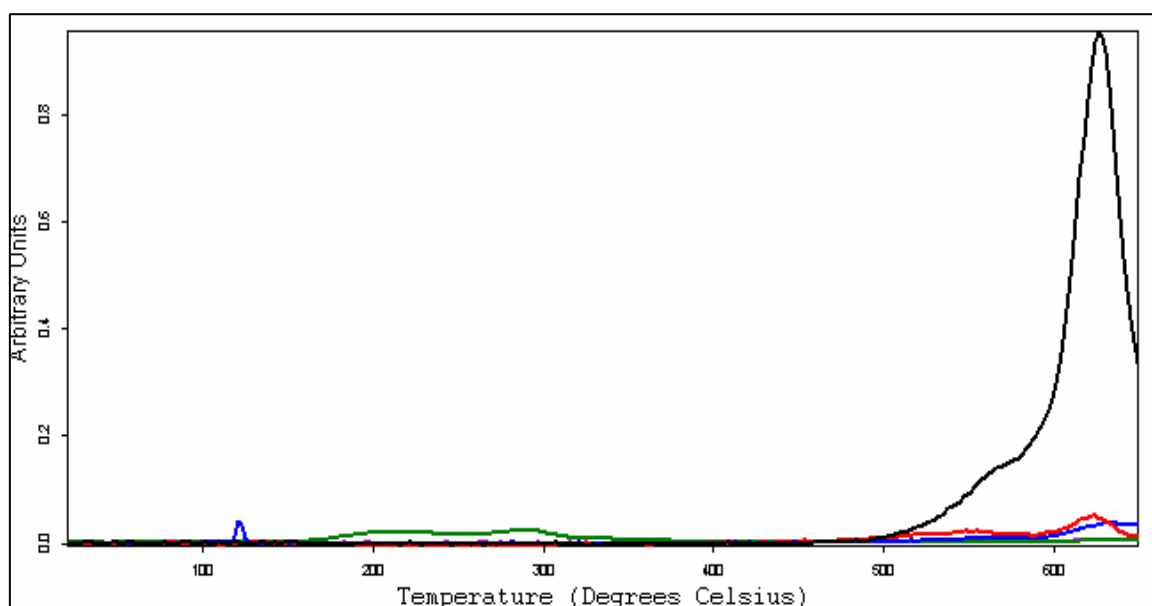
DISTRIBUTION LIST

Catalytic Degradation of Methylphosphonic Acid Using Iron Powder / Iron Oxides

Joseph John Moniodis, John Webb, Gary Mathys, Harry Rose and Robert Mathews

AUSTRALIA

DEFENCE ORGANISATION

	No. of copies
Task Sponsor	1 Printed
ASSIER	
DSOCAUST	1 Printed
CO IRR	1 Printed

S&T Program	
Chief Defence Scientist	1
Deputy Chief Defence Scientist Policy	1
AS Science Corporate Management	1
Director General Science Policy Development	1
Counsellor Defence Science, London	Doc Data Sheet
Counsellor Defence Science, Washington	Doc Data Sheet
Scientific Adviser to MRDC, Thailand	Doc Data Sheet
Scientific Adviser Joint	1
Navy Scientific Adviser	1
Scientific Adviser – Army	1
Air Force Scientific Adviser	1
Scientific Adviser to the DMO	1

Platforms Sciences Laboratory	
Chief of Human Protection & Performance Division	Doc Data Sht & Dist List
Head : Dr. Robert Mathews	1 Printed
Task Manager: Dr Harry Rose	1 Printed
Gary Mathys	1 Printed
Dr. John Webb	1 Printed
Joseph John Moniodis	1 Printed

DSTO Library and Archives	
Library Fishermans Bend	1 printed
Library Edinburgh	1 printed
Defence Archives	1 printed

Capability Development Group	
Director General Maritime Development	Doc Data Sheet
Director General Land Development	1

Director General Capability and Plans	Doc Data Sheet
Assistant Secretary Investment Analysis	Doc Data Sheet
Director Capability Plans and Programming	Doc Data Sheet

Chief Information Officer Group

Director General Australian Defence Simulation Office	Doc Data Sheet
AS Information Strategy and Futures	Doc Data Sheet
Director General Information Services	Doc Data Sheet

Strategy Group

Director General Military Strategy	Doc Data Sheet
Assistant Secretary Governance and Counter-Proliferation	Doc Data Sheet

Navy

Maritime Operational Analysis Centre, Building 89/90 Garden Island Sydney NSW	Doc Data Sht & Dist List
Deputy Director (Operations)	
Deputy Director (Analysis)	
Director General Navy Capability, Performance and Plans, Navy Headquarters	Doc Data Sheet
Director General Navy Strategic Policy and Futures, Navy Headquarters	Doc Data Sheet

Air Force

SO (Science) - Headquarters Air Combat Group, RAAF Base, Williamtown NSW 2314	Doc Data Sht & Exec Summary

Army

ABCA National Standardisation Officer	e-mailed Doc Data Sheet
Land Warfare Development Sector, Puckapunyal	
SO (Science) - Land Headquarters (LHQ), Victoria Barracks NSW	Doc Data & Exec Summary
SO (Science), Deployable Joint Force Headquarters (DJFHQ) (L), Enoggera QLD	Doc Data Sheet

Joint Operations Command

Director General Joint Operations	Doc Data Sheet
Chief of Staff Headquarters Joint Operations Command	Doc Data Sheet
Commandant ADF Warfare Centre	Doc Data Sheet
Director General Strategic Logistics	Doc Data Sheet
COS Australian Defence College	Doc Data Sheet

Intelligence and Security Group

AS Concepts, Capability and Resources	1
DGSTA , Defence Intelligence Organisation	1
Manager, Information Centre, Defence Intelligence Organisation	1
Director Advanced Capabilities	Doc Data Sheet

Defence Materiel Organisation

Deputy CEO	Doc Data Sheet
Head Aerospace Systems Division	Doc Data Sheet

Head Maritime Systems Division	Doc Data Sheet
Program Manager Air Warfare Destroyer	Doc Data Sheet
CDR Joint Logistics Command	Doc Data Sheet
Guided Weapon & Explosive Ordnance Branch (GWEO)	Doc Data Sheet

OTHER ORGANISATIONS

National Library of Australia	1
NASA (Canberra)	1
Library of New South Wales	1

UNIVERSITIES AND COLLEGES

Australian Defence Force Academy

Library	1
Head of Aerospace and Mechanical Engineering	1
Hargrave Library, Monash University	Doc Data Sheet

OUTSIDE AUSTRALIA

INTERNATIONAL DEFENCE INFORMATION CENTRES

US Defense Technical Information Center	1
UK Dstl Knowledge Services	1
Canada Defence Research Directorate R&D Knowledge & Information Management (DRDKIM)	1
NZ Defence Information Centre	1

ABSTRACTING AND INFORMATION ORGANISATIONS

Library, Chemical Abstracts Reference Service	1
Engineering Societies Library, US	1
Materials Information, Cambridge Scientific Abstracts, US	1
Documents Librarian, The Center for Research Libraries, US	1
SPARES	5 Printed

Total number of copies: 42   Printed: 16   PDF: 26

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION DOCUMENT CONTROL DATA		1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)	

<table>
<tr>
<td colspan="2">2. TITLE

Catalytic Degradation of Methylphosphonic Acid Using Iron Powder/ Iron Oxides</td>
<td colspan="2">3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)

    Document   (U)
    Title   (U)
    Abstract   (U)</td>
</tr>
<tr>
<td colspan="2">4. AUTHOR(S)

Joseph John Moniodis, John Webb, Gary Mathys, Harry Rose and Robert Mathews</td>
<td colspan="2">5. CORPORATE AUTHOR

DSTO Defence Science and Technology Organisation
506 Lorimer St
Fishermans Bend Victoria 3207 Australia</td>
</tr>
<tr>
<td>6a. DSTO NUMBER
DSTO-TR-1849</td>
<td>6b. AR NUMBER
AR-013-627</td>
<td>6c. TYPE OF REPORT
Technical Report</td>
<td>7. DOCUMENT DATE
November 2005</td>
</tr>
</table>

8. FILE NUMBER 2004/ 1029011	9. TASK NUMBER ARM 02/109	10. TASK SPONSOR CMMD LWDC	11. NO. OF PAGES 37	12. NO. OF REFERENCES 34

| 13. URL on the World Wide Web

http://www.dsto.defence.gov.au/corporate/reports/DSTO-TR-1849.pdf | 14. RELEASE AUTHORITY

Chief, Human Protection and Performance Division |
|---|---|

15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for public release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE, PO BOX 1500, EDINBURGH, SA 5111

16. DELIBERATE ANNOUNCEMENT

No Limitations

17. CITATION IN OTHER DOCUMENTS	Yes

18. DSTO RESEARCH LIBRARY THESAURUS

Chemical agents, Chemical weapons, Nerve agents, Degradation

19. ABSTRACT

The catalytic degradation of methylphosphonic acid, the final hydrolysis product of some nerve agents, using Fe, Fe_2O_3, $FePO_4$ and Al/Al_2O_3 was studied by evolved gas analysis - Fourier transform infrared spectroscopy (EGA-FTIR) under nitrogen, air and oxygen atmospheres. All of the compounds catalysed the reaction to some extent (in comparison to heating MPA alone) with Fe_2O_3 being the best catalyst with carbon-containing gases evolving at 375°C under all atmospheres. Temperatures of formation of carbon containing gases using the other catalysts were 400-450°C for Fe, 400-425°C for $FePO_4$ and ca. 510°C for Al/Al_2O_3. There is some evidence that Fe and Fe_2O_3 reacted with MPA to form an iron phosphate species, which further catalysed the reaction although to a lesser extent.